

## CLAIMS

1. A method of forming material on a substrate, comprising:
  - positioning a substrate within a deposition chamber;
  - chemisorbing a first species monolayer onto the substrate within the chamber from a gaseous first precursor, the first species monolayer being discontinuously formed over the substrate;
  - exposing the substrate having the discontinuous first species monolayer to a gaseous second precursor different from the first precursor effective to react with the first species to form a second species monolayer and effective to form a reaction product of the second precursor with substrate material not covered by the first species monolayer; and
  - exposing the substrate having the second species monolayer and the reaction product to a third gaseous substance different from the first and second precursors effective to selectively remove the reaction product from the substrate relative to the second species monolayer.
2. The method of claim 1 wherein the reaction product is silicon dioxide formed from reaction of the gaseous second precursor with silicon substrate material.

3. The method of claim 2 wherein the third gaseous substance comprises a halide.

4. The method of claim 2 wherein the third gaseous substance comprises a hydrogen halide.

5. The method of claim 2 wherein the third gaseous substance comprises fluorine.

6. The method of claim 1 wherein the reaction product and second species each comprise an oxide.

7. The method of claim 6 wherein each of the reaction product and the second species respectively comprises a dioxide.

8. The method of claim 6 wherein the reaction product comprises a dioxide and the second species monolayer comprises an oxide other than a dioxide.

9. The method of claim 1 wherein the gaseous first precursor and the first species monolayer comprise hafnium.

10. The method of claim 1 wherein the gaseous first precursor and the first species monolayer comprise hafnium, the second precursor comprises oxygen, and the second species monolayer comprises an oxide of hafnium.

11. The method of claim 1 wherein the gaseous first precursor and the first species monolayer comprise aluminum.

12. The method of claim 1 wherein the gaseous first precursor and the first species monolayer comprise aluminum, the second precursor comprises oxygen, and the second species monolayer comprises an oxide of aluminum.

13. The method of claim 1 further comprising after conducting a cycle of the chemisorbing, the exposing to the second gaseous precursor and the exposing to the third gaseous substance, exposing the substrate to the first gaseous precursor, then the second gaseous precursor and without exposing the substrate to the third gaseous substance for at least one cycle.

14. The method of claim 1 further comprising repeating the chemisorbing, the exposing to the second gaseous precursor and the exposing to the third gaseous substance.

15. The method of claim 14 further comprising after said repeating at least one cycle, exposing the substrate to the first gaseous precursor, then the second gaseous precursor and without exposing the substrate to the third gaseous substance for at least one cycle.

16. The method of claim 14 wherein the first gaseous precursor during said repeated chemisorbing preferentially adsorbs to substrate material other than the second species monolayer.

17. The method of claim 16 wherein said preferentially adsorbing is at a ratio of at least 2:1.

18. The method of claim 16 wherein said preferential adsorbing is apparent at conclusion of said repeated chemisorbing.

19. A method of forming a field effect transistor gate oxide on a substrate, comprising:

- positioning a substrate within a deposition chamber;
- chemisorbing a first metal containing species monolayer onto the substrate within the chamber from a gaseous first precursor, the first metal containing species monolayer being discontinuously formed over the substrate;
- exposing the substrate having the discontinuous first metal containing species monolayer to a gaseous oxygen containing second precursor different from the first precursor effective to react with the first metal containing species to form a gate dielectric second metal oxide monolayer and effective to form an oxide reaction product of the oxygen containing second precursor with substrate material not covered by the first metal containing species monolayer; and
- exposing the substrate having the gate dielectric second metal oxide monolayer and the oxide reaction product to a halogen containing third gaseous substance different from the first and second precursors effective to selectively remove the oxide reaction product from the substrate relative to the gate dielectric second metal oxide monolayer.

20. The method of claim 19 wherein the oxide reaction product is silicon dioxide formed from reaction of the gaseous oxygen containing second precursor with silicon substrate material.

21. The method of claim 19 wherein the third gaseous substance comprises a hydrogen halide.

22. The method of claim 19 wherein the halogen comprises fluorine.

23. The method of claim 19 wherein each of the oxide reaction product and the second species respectively comprises a dioxide.

24. The method of claim 19 wherein the oxide reaction product comprises a dioxide and the second metal oxide monolayer comprises an oxide other than a dioxide.

25. The method of claim 19 wherein the gaseous first precursor and the first metal containing species monolayer comprise hafnium, and the second metal oxide monolayer comprises an oxide of hafnium.

26. The method of claim 19 wherein the gaseous first precursor and the first metal containing species monolayer comprise aluminum, and the second metal oxide monolayer comprises an oxide of aluminum.

27. The method of claim 19 further comprising after conducting a cycle of the chemisorbing, the exposing to the gaseous oxygen containing second precursor and the exposing to the halogen containing third gaseous substance, exposing the substrate to the first gaseous precursor, then the second gaseous precursor and without exposing the substrate to the third gaseous substance for at least one cycle.

28. A method of forming material on a substrate, comprising:  
positioning a substrate within a deposition chamber;  
chemisorbing a first species monolayer onto the substrate within the chamber from a gaseous precursor "a";  
exposing the substrate having the first species monolayer to a gaseous precursor "b" different from precursor "a" effective to react with the first species to form a second species monolayer, the exposing leaving some undesired impurity remaining on the substrate; and  
exposing the substrate having the undesired impurity to a gaseous substance "c" different from the precursors "a" and "b" effective to selectively remove the undesired impurity from the substrate relative to the second species monolayer.

29. The method of claim 28 wherein the first species monolayer is discontinuously formed over the substrate prior to the exposing to the gaseous precursor "b".

30. The method of claim 28 wherein the undesired impurity remaining on the substrate is derived from the first species monolayer.

31. The method of claim 28 wherein the undesired impurity remaining on the substrate is carbon derived from the first species monolayer.

32. The method of claim 28 wherein the undesired impurity remaining on the substrate is carbon derived from the first species monolayer, and gaseous substance "c" comprises a hydrogen halide.

33. The method of claim 28 wherein the undesired impurity remaining on the substrate is carbon derived from the first species monolayer, and gaseous substance "c" comprises fluorine.

34. The method of claim 28 wherein the undesired impurity remaining on the substrate is a halogen derived from the first species monolayer.



35. The method of claim 28 wherein the undesired impurity remaining on the substrate is a halogen derived from the first species monolayer, and gaseous substance "c" comprises  $H_2$ .

36. The method of claim 28 wherein the undesired impurity remaining on the substrate is a halogen derived from the first species monolayer, and gaseous substance "c" comprises diborane.

37. The method of claim 28 wherein the undesired impurity remaining on the substrate is a halogen derived from the first species monolayer, and gaseous substance "c" comprises hydrazine.

38. The method of claim 28 wherein the material comprises  $Al_2O_3$ , gaseous precursor "a" comprises trimethylaluminum, gaseous second precursor "b" comprises oxygen, the undesired impurity comprises carbon, and gaseous substance "c" comprises a halogen.

39. The method of claim 38 wherein gaseous substance "c" comprises a hydrogen halide.

40. The method of claim 28 wherein the material comprises TiN, a gaseous precursor "a" comprises  $\text{TiCl}_4$ , gaseous second precursor "b" comprises ammonia, the undesired impurity comprises chlorine, and gaseous substance "c" comprises  $\text{H}_2$ .

41. The method of claim 28 wherein the material comprises TiN, a gaseous precursor "a" comprises  $\text{TiCl}_4$ , gaseous second precursor "b" comprises ammonia, the undesired impurity comprises chlorine, and gaseous substance "c" comprises diborane.

42. The method of claim 28 wherein the material comprises TiN, a gaseous precursor "a" comprises  $\text{TiCl}_4$ , gaseous second precursor "b" comprises ammonia, the undesired impurity comprises chlorine, and gaseous substance "c" comprises hydrazine.

43. The method of claim 28 further comprising after exposing the substrate to gaseous substance "c", exposing the substrate to a gaseous substance "d" different from "a", "b" and "c" effective to remove a reaction product from the substrate formed by exposure to "c".